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(54) Title: STABILIZATION OF METHYLMETHACRYLATE-BUTADIENE-STYRENE GRAFT COPOLYMERS AGAINST THERMAL OXIDATION

(57) Abstract: The instant invention relates to a stabilized composition of methylmethacrylate-butadiene-styrene graft copolymers with selected sterically hindered phenolic antioxidants and thioethers. Further subjects of the invention are a process for the stabilization of methylmethacrylate-butadiene-styrene graft copolymers and the use of selected sterically hindered phenolic antioxidants together with a thioether for the thermal stabilization of said graft copolymer.

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Stabilization of Methylmethacrylate-Butadiene-Styrene Graft Copolymers against Thermal Oxidation

The instant invention relates to a stabilized composition of methylmethacrylate-butadiene-styrene graft copolymers with selected sterically hindered phenolic antioxidants and

5 thioethers. Further subjects of the invention are a process for the stabilization of methylmethacrylate-butadiene-styrene graft copolymers and the use of selected sterically hindered phenolic antioxidants together with a thioether for the thermal stabilization of said graft copolymer.

10 Polymers having a grafted polybutadiene or polybutadiene-styrene rubber phase, such as ABS (acrylonitrile-butadiene-styrene), or MBS (methylmethacrylate-butadiene-styrene) are very prone to oxidative degradation of the rubber phase, especially under the influence of heat and oxygen. This is especially problematic during air-drying of ABS- or MBS-graft-phase powders. MBS is even more prone to oxidation and, therefore, more difficult to stabilize
15 because it has usually a higher rubber content than ABS, and a smaller particle size of the graft-phase powder (higher surface area). The stability of MBS powder is generally much lower than that of ABS.

State of the art in the stabilization of MBS against thermal oxidation, is the use of
20 combinations of hindered phenolic antioxidants in combination with thioethers. Typical hindered phenolic antioxidants are, BHT, @Topanol CA, @CIBA @Irganox 1076, @CIBA @Irganox 245, @CIBA @Irganox 1141, etc. As thioethers, usually DLTD (di-lauryl-thio-di-propionate) or DSTDP (di-stearyl-thio-di-propionate) are used. To adequately protect the MBS during the drying step, much higher concentrations of these stabilizers have to be used
25 than in ABS. However, very high concentrations of hindered phenolic antioxidants and thioethers can lead to color formation during processing and end use, due to over-oxidation of the hindered phenolic antioxidants and subsequent formation of highly colored quinoid structures. Therefore, more efficient stabilizer packages for MBS are required that do not need such a high dosage.

30 Surprisingly it has been found that some very specific hindered phenolic antioxidants, such as @Wingstay L, @CIBA @Irganox 415 or @CIBA @Irganox 3790 show especially good performance in MBS versus the above mentioned prior art stabilizers. Although the excellent

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performance of @Wingstay L and @CIBA @Irganox 415 is well established in ABS, so far neither @Wingstay L, @CIBA @Irganox 415 nor @CIBA @Irganox 3790, have been used for pure MBS stabilization.

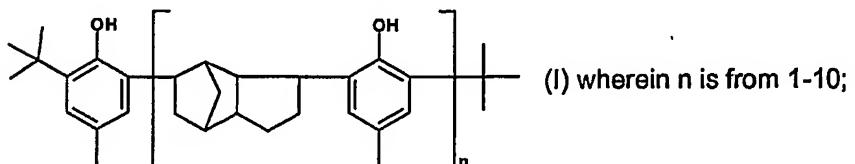
Although MBS seems to be a similar polymer as ABS, it nevertheless behaves very
5 differently in terms of stabilization against thermal oxidation. Besides the above already mentioned, generally much lower thermal stability of MBS compared to ABS, the following differences are noteworthy.

ABS can be stabilized with hindered phenol antioxidants alone, or with combinations of
10 hindered phenol antioxidants and thioethers (DLTDP, DSTDP). MBS, on the other hand, cannot be stabilized with hindered phenol antioxidants alone. Only combinations with thioethers provide sufficient stability.

In view of the considerable differences between MBS and ABS, it is surprising that
15 combinations of @Wingstay L, @CIBA @Irganox 415, or @CIBA @Irganox 3790 and thioethers show the best performance in MBS.

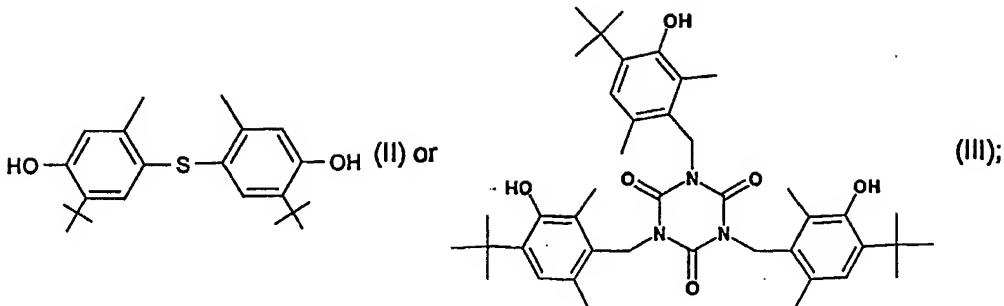
One aspect of the invention is a stabilized polymer composition comprising

- 20 a) a polymer, which is a graft copolymer of methylmethacrylate and styrene on polybutadiene or polybutadiene-styrene (methylmethacrylate-styrene-butadiene graft copolymer MBS);
b) a sterically hindered phenolic antioxidant of formula (I), (II) or (III) or a mixture thereof



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and

- c) a thioether differing from that of formula (II);

with the proviso, that no other styrene polymer or copolymer, which is not a graft copolymer.

5 on butadiene is present.

MBS is a commercial graft latex, which can, for example, be prepared according to EP 0 488 550.

10 The above stabilized polymer composition may be in the form of a latex, i. e. the composition contains a water phase. Preferably the stabilized polymer composition is, however, in the solid state.

For instance the stabilized polymer composition is in the form of a powder or granulate.

15

The compounds according to formulae (I), (II) and (III) are commercial compounds.

The compound of formula (I) is bis(3-tert-butyl-4-hydroxy-5-methyl-phenyl)dicyclopentadiene commercialised as Wingstay® L from Eliokem or Ralox® LC from Raschig. In the commercial compounds the mean value of n in formula (I) is approximately 1.

The compound of formula (II) is 4,4' thiobis(6-tert-butyl-3-methylphenol), commercialised as
©CIBA ©Irganox 415 from Ciba Specialty Chemicals Inc.

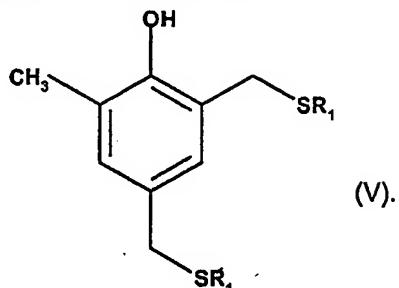
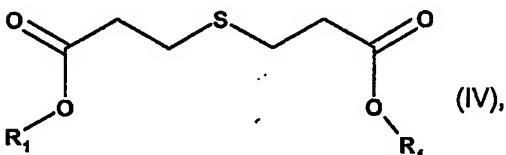
25 The compound of formula (III) is 1,3,5-tris [4-(1,1-dimethylethyl)-3-hydroxy-2,6-dimethylphenyl] methyl]- 1,3,5 -triazine-2,4,6(1H,3H,5H)-trione, or 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate commercialized as ®CIBA ®Irganox 3790 from Ciba Specialty Chemicals Inc.

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The compound of formula (I) is most preferred.

In a specific embodiment the thioether is a compound of formula (IV) or (V)

5



wherein the R₁ are independently C₈-C₂₀alkyl.

Specific compounds according to formula (IV) are di-lauryl-thio-di-propionate and di stearyl-thio-di-propionate, which are commercial products of Ciba Specialty Chemicals Inc. with the
10 trade names @CIBA Irganox® PS 800 and @CIBA Irganox® PS 802. The compound of formula (V) with R₁ = C₈alkyl is also a commercial product of Ciba Specialty Chemicals Inc.
and sold under the trade name @CIBA Irganox® 1520.

For example the sterically hindered phenolic antioxidant is present in an amount of 0.05 to
15 1% based on the weight of the dry graft copolymer, component a).

For instance the thioether is present in an amount of 0.1 to 5%, preferably from 0.1 to 3% based on the weight of the dry graft copolymer, component a).

20 Preferably the ratio of sterically hindered phenolic antioxidant to thioether is from 1:1 to 1:5, more preferably from 1:2 to 1:4.

In a specific embodiment the stabilized polymer composition comprises additionally a further
25 sterically hindered phenolic antioxidant different from those of formulae (I), (II) or (III), a phosphite process stabilizer, a UV-absorber, a sterically hindered amine light stabilizer, a metal deactivator, an acid scavenger, a metal salt of a fatty acid, a fluorescent whitening agent, a biocide or a surfactant.

Examples of the additional components are given below.

1. Antioxidants

1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-di-

5 methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

10 1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.

15

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadeoxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

1.4. Tocopherols, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures thereof (vitamin E).

25 1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl)disulfide.

30 1.6. Alkyldenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)-phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α , α -dimethylbenzyl)-4-nonylphenol], 4,4'-methyl-

lenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptopbutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptopbutane, 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

10 1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydi-benzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isoctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

15 1.8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, di-dodecylmercaptoethyl-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

20 1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

25 1.10. Triazine compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

30 1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-tert-butyl-4-hy-

droxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.

1.12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-

- 5 **(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.**

1.13. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric

alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-
nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiidiethylene glycol, diethy-

- 10 **lene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hy-
droxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylol-
propane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.**

1.14. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or poly-

15 **hydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanedi-
ol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiidiethylene glycol,**

**diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis-
(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethyl-**

- 20 **olpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane; 3,9-bis[2-{3-(3-tert-
butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5.5]-
undecane.**

1.15. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric

alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol,
25 **ethylene glycol, 1,2-propanediol, neopentyl glycol, thiidiethylene glycol, diethylene glycol, tri-**

**ethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)ox-
amide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hy-
droxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.**

- 30 **1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alco-**

**hols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol,
ethylene glycol, 1,2-propanediol, neopentyl glycol, thiidiethylene glycol, diethylene glycol,
triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)ox-**

amide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospho-2,6,7-trioxabicyclo[2.2.2]octane.

1.17. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-

5 butyl-4-hydroxyphenylpropionyl)hexamethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxy-phenylpropionyl)trimethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazide, N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyloxy)ethyl]oxamide (Nau-gard[®]XL-1, supplied by Uniroyal).

10 1.18. Ascorbic acid (vitamin C)

1.19. Aminic antioxidants, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-sec-bu-

5 tyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfamoyl)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylamino-methylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetra-25 methyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2-bis(phenyl-amino)propane, (o-tolyl)biguanide, bis[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isohexyl-diphenylamines, a mixture of mono- and dialkylated tert-butylidiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- and dialkylated tert-octylphenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetra-

- 9 -

methylpiperid-4-yl-hexamethylenediamine, bis(2,2,6,6-tetramethylpiperid-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

2. UV absorbers and light stabilisers

5

2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis(α,α -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenylbenzotriazole, 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-ylphenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol

300; $[R-\text{CH}_2\text{CH}_2-\text{COO}-\text{CH}_2\text{CH}_2]_2$, where R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotri-

azol-2-ylphenyl, 2-[2'-hydroxy-3'-(α,α -dimethylbenzyl)-5'-(1,1,3,3-tetramethylbutyl)phenyl]-benzotriazole; 2-[2'-hydroxy-3'-(1,1,3,3-tetramethylbutyl)-5'-(α,α -dimethylbenzyl)phenyl]ben-

25 zotriazole.

2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

30 **2.3. Esters of substituted and unsubstituted benzoic acids**, for example 4-tert-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzo-

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ate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl α -cyano- β,β -diphenylacrylate, isooctyl α -cyano- β,β -diphe-

5 nylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl-p-methoxycinnamate, butyl α -cyano- β -methyl-p-methoxycinnamate, methyl α -carbomethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thiobis[4-(1,1,3,3-tetramethyl-

10 butyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphenylundecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate,

bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate,

bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperi-

20 dyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-di-chloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitrilotriacetate, tetrakis(2,2,6,6-tetra-

25 methyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetra-methylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethyl-piperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)-

30 malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyl-oxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succi-

nate, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylene-

diamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)-ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-

1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetra-

methoxy-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyr-

rolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine, a condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensate of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); a condensate of 1,6-hexanediamine and 2,4,6-trichloro-1,3,5-triazine as well as N,N-dibutylamine and 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [192268-64-7]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane, a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro-[4,5]decane and epichlorohydrin, 1,1-bis(1,2,2,6,6-pentamethyl-4-piperidyl)hexamethylenediamine, a diester of 4-methoxymethylenemalonic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, poly[methylpropyl-3-oxy-4-(2,2,6,6-tetramethyl-4-piperidyl)]siloxane, a reaction product of maleic acid anhydride- α -olefin copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine.

2.7. Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide, mixtures of o- and p-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyl-oxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)phenyl]-4,6-bis(2,4-dimethyl-phenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hy-

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droxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine, 2-[2-hydroxy-4-[3-(2-ethylhexyl-1-oxy)-2-hydroxypropyloxy]phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

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3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl)hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxaryl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacyl bisphenylhydrazide, N,N'-diacetyl dipoyl dihydrazide, N,N'-bis(salicyloyl)oxaryl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.

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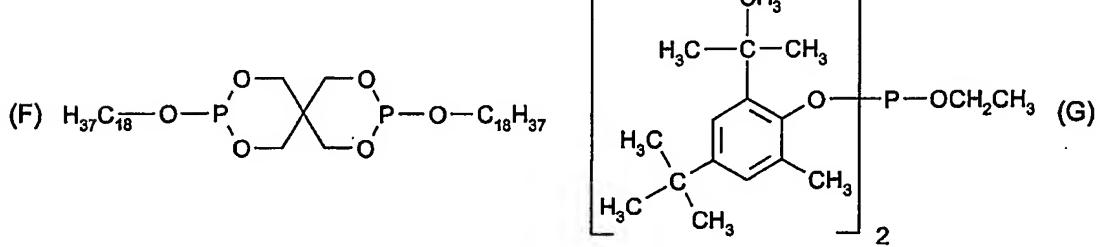
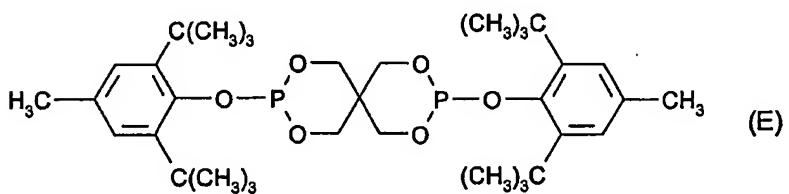
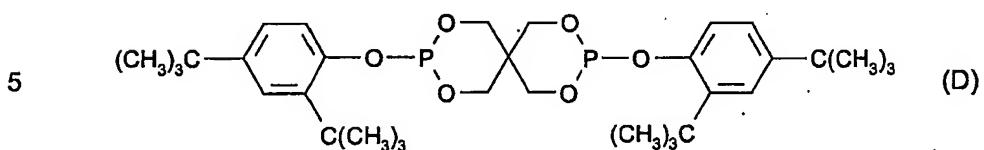
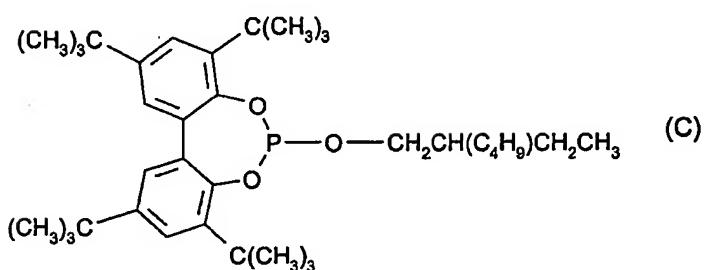
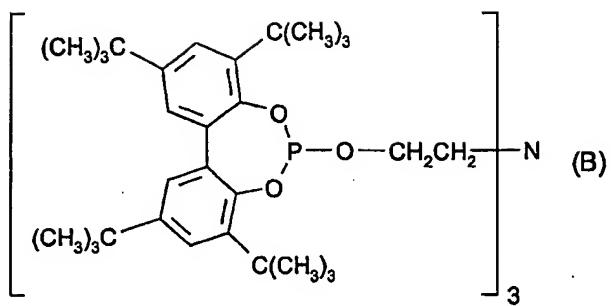
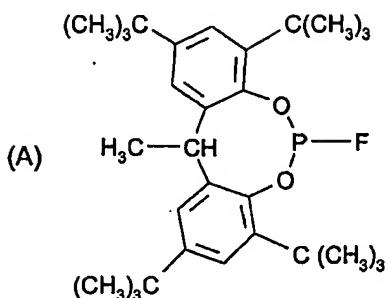
4. Phosphites and phosphonites, for example triphenyl phosphite, diphenylalkyl phosphites, phenyldialkyl phosphites, tris(nonylphenyl) phosphite, triauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, bis(2,4-di-cumylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite, diisodecyloxy pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl)pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-isoctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl)methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl)ethyl phosphite, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, 2,2',2"-nitrilo-[triethyltris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite], 2-ethylhexyl(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite, 5-butyl-5-ethyl-2-(2,4,6-tri-tert-butylphenoxy)-1,3,2-dioxaphosphirane.

The following phosphites are especially preferred:

Tris(2,4-di-tert-butylphenyl) phosphite (@CIBA @Irgafos168, Ciba Specialty Chemicals),

30 tris(nonylphenyl) phosphite,

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- 5 5. Hydroxylamines, for example N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-diethylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.
- 10 6. Nitrones, for example N-benzyl-alpha-phenylnitrone, N-ethyl-alpha-methylnitrone, N-octyl-alpha-heptylnitrone, N-lauryl-alpha-undecylnitrone, N-tetradecyl-alpha-tridecylnitrone, N-hexadecyl-alpha-pentadecylnitrone, N-octadecyl-alpha-heptadecylnitrone, N-hexadecyl-alpha-heptadecylnitrone, N-octadecyl-alpha-pentadecylnitrone, N-heptadecyl-alpha-heptadecylnitrone, N-octadecyl-alpha-hexadecylnitrone, nitrone derived from N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.
- 15 7. Peroxide scavengers, for example esters of β -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptopbenzimidazole, zinc dibutylthiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis(β -dodecylmercapto)propionate.
- 20 8. Basic co-stabilisers, for example melamine, polyvinylpyrrolidone, dicyandiamide, triallycyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids, for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or zinc pyrocatecholate.
- 25 9. Nucleating agents, for example inorganic substances, such as talcum, metal oxides, such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, alkaline earth metals; organic compounds, such as mono- or polycarboxylic acids and the salts thereof, e.g. 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid, sodium succinate or sodium benzoate; polymeric compounds, such as ionic copolymers (ionomers). Especially preferred are 1,3:2,4-bis(3',4'-dimethylbenzylidene)sorbitol, 1,3:2,4-di(paramethyldibenzylidene)sorbitol, and 1,3:2,4-di(benzylidene)sorbitol.

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10. Fillers and reinforcing agents, for example calcium carbonate, silicates, glass fibres, glass bulbs, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood flour and flours or fibers of other natural products, synthetic fibers.

5 11. Other additives, for example plasticisers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing agents, antistatic agents and blowing agents.

10 12. Benzofuranones and indolinones, for example those disclosed in U.S. 4,325,863; U.S. 4,338,244; U.S. 5,175,312; U.S. 5,216,052; U.S. 5,252,643; DE-A-4316611; DE-A-4316622; DE-A-4316876; EP-A-0589839 or EP-A-0591102 or 3-[4-(2-acetoxyethoxy)-phenyl]-5,7-di-tert-butylbenzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]-benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-15 di-tert-butylbenzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butylbenzo-furan-2-one, 3-(3,4-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(2,3-dimethylphe-nyl)-5,7-di-tert-butylbenzofuran-2-one.

20 13. Acid scavengers: organic acid scavengers, e.g. epoxidised soy bean oil (ESBO), or inorganic bases, e.g. NaOH, KOH, Ca(OH)₂, etc.

Specific examples of compositions are:

A MBS latex and

25 Wingstay® L, ®CIBA Irganox® 415 or ®CIBA Irganox® 3790, or combinations thereof di-lauryl-thio-di-propionate (®CIBA Irganox® PS 800 = DLTDP) or di-stearyl-thio-di-propionate (®CIBA Irganox® PS 802 = DSTDP) or ®CIBA Irganox® 1520; other hindered phenolic antioxidants, such as ®CIBA Irganox® 245, ®CIBA Irganox® 1076 and combinations thereof; and
30 potassium or sodium oleate, potassium or sodium stearate.

A MBS latex and

Wingstay® L, or ®CIBA Irganox® 415, or ®CIBA Irganox® 3790, or combinations thereof

di-lauryl-thio-di-propionate (@CIBA Irganox® PS 800 = DLTDP) or @CIBA Irganox® 1520 and potassium oleate.

- 5 Both specific compositions are in the latex form containing water.

Both specific compositions may also be in the solid state, for example as powder or granulate.

- 10 Another aspect of the invention is a process for the stabilization of a graft copolymer of methylmethacrylate and styrene on polybutadiene or polybutadiene-styrene (methylmethacrylate-styrene-butadiene graft copolymer MBS) where no other styrene polymer or copolymer, which is not a graft copolymer on butadiene is present, comprising the steps
- 15 a) adding to the MBS latex a sterically hindered phenolic antioxidant of formula (I), (II) or (III) and a thioether as outlined above;
- b) coagulating the MBS latex and
- c) drying the MBS latex at elevated temperature.
- 20 The sterically hindered phenolic antioxidant of formula (I), (II) or (III) and the thioether may be added individually or together. They are admixed to the latex by conventional means, such as for example stirrers. The preparation of a stabilized latex is for example described in US 5,116,534.
- 25 The coagulating step is a known process, which may be carried out as, for example, described in EP 0 488 550. Specifically, acids (e.g. hydrochloric or sulphuric acid) or inorganic salts (e.g. magnesium sulfate or calcium chloride) can be used as coagulating agents.
- 30 Typically the drying step is carried out at a temperature of 40° C to 150° C, preferably at a temperature of 50° C to 80° C.

In many cases it may be useful to carry out the drying step under reduced pressure, such as for example from 10 mbar to 500 mbar. To accelerate the drying step an additional air or nitrogen flow may be applied. Typical drying times are from 1 hour to 24 hours.

- 5 As alternative to coagulation, the MBS graft copolymer can also be isolated by freeze or spray drying.

Yet another aspect of the invention is the use of a sterically hindered phenolic antioxidant of formula (I), (II) or (III) together with a thioether for the stabilization of a graft copolymer of 10 methylmethacrylate and styrene on polybutadiene or polybutadiene-styrene (methylmethacrylate-styrene-butadiene graft copolymer MBS) where no other styrene polymer or copolymer, which is not a graft copolymer on butadiene is present.

Definitions and preferences given above for the composition apply also for the other aspects 15 of the invention.

The stabilized MBS in latex form or as dried granulate or powder is useful as impact modifier for thermoplastic or elastomeric polymers.

- 20 Examples of polymers in which the stabilized MBS in dried form or as latex may be incorporated are given below.

1. Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-1-ene, polyvinylcyclohexane, polyisoprene or polybutadiene, 25 as well as polymers of cycloolefins, for instance of cyclopentene or norbornene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight polyethylene (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), (VLDPE) and 30 (ULDPE).

Polyolefins, i.e. the polymers of monoolefins exemplified in the preceding paragraph, preferably polyethylene and polypropylene, can be prepared by different, and especially by the following, methods:

- a) radical polymerisation (normally under high pressure and at elevated temperature).
- b) catalytic polymerisation using a catalyst that normally contains one or more than one metal of groups IVb, Vb, VIb or VIII of the Periodic Table. These metals usually have one or more than one ligand, typically oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls that may be either π - or σ -coordinated. These metal complexes may be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium(III) chloride, alumina or silicon oxide. These catalysts may be soluble or insoluble in the polymerisation medium. The catalysts can be used by themselves in the polymerisation or further activators may be used, typically metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyloxanes, said metals being elements of groups Ia, IIa and/or IIIa of the Periodic Table. The activators may be modified conveniently with further ester, ether, amine or silyl ether groups. These catalyst systems are usually termed Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC).
2. Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).
3. Copolymers of monoolefins and diolefins with each other or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, propylene/isobutylene copolymers, ethylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, ethylene/vinylcyclohexane copolymers, ethylene/cycloolefin copolymers (e.g. ethylene/norbornene like COC), ethylene/1-olefins copolymers, where the 1-olefin is generated in-situ; propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/vinylcyclohexene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers or ethylene/acrylic acid copolymers and their salts (ionomers) as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethyldene-norbornene; and mixtures of such copolymers

with one another and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LLDPE/EVA, LLDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example
5 polyamides.

4. Hydrocarbon resins (for example C₅-C₉) including hydrogenated modifications thereof (e.g. tackifiers) and mixtures of polyalkylenes and starch.
- 10 Homopolymers and copolymers from 1.) - 4.) may have any stereostructure including syndiotactic, isotactic, hemi-isotactic or atactic; where atactic polymers are preferred. Stereoblock polymers are also included.
- 15 5. Polystyrene, poly(p-methylstyrene), poly(α -methylstyrene).
- 20 6. Aromatic homopolymers and copolymers derived from vinyl aromatic monomers including styrene, α -methylstyrene, all isomers of vinyl toluene, especially p-vinyltoluene, all isomers of ethyl styrene, propyl styrene, vinyl biphenyl, vinyl naphthalene, and vinyl anthracene, and mixtures thereof. Homopolymers and copolymers may have any stereostructure including syndiotactic, isotactic, hemi-isotactic or atactic; where atactic polymers are preferred. Stereoblock polymers are also included.
- 25 6a. Copolymers including aforementioned vinyl aromatic monomers and comonomers selected from ethylene, propylene, dienes, nitriles, acids, maleic anhydrides, maleimides, vinyl acetate and vinyl chloride or acrylic derivatives and mixtures thereof, for example styrene/butadiene, styrene/acrylonitrile, styrene/ethylene (interpolymers), styrene/alkyl methacrylate, styrene/butadiene/alkyl acrylate, styrene/butadiene/alkyl methacrylate, styrene/maleic anhydride, styrene/acrylonitrile/methyl acrylate; mixtures of high impact strength of styrene copolymers and another polymer, for example a polyacrylate, a diene polymer or an ethylene/propylene/diene terpolymer; and block copolymers of styrene such as styrene/butadiene/styrene, styrene/isoprene/styrene, styrene/ethylene/butylene/styrene or styrene/ethylene/propylene/styrene.

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- 6b. Hydrogenated aromatic polymers derived from hydrogenation of polymers mentioned under 6.), especially including polycyclohexylethylene (PCHE) prepared by hydrogenating atactic polystyrene, often referred to as polyvinylcyclohexane (PVCH).
- 5 6c. Hydrogenated aromatic polymers derived from hydrogenation of polymers mentioned under 6a.).
- Homopolymers and copolymers may have any stereostructure including syndiotactic, isotactic, hemi-isotactic or atactic; where atactic polymers are preferred. Stereoblock polymers are
10 also included.
7. Halogen-containing polymers such as polychloroprene, chlorinated rubbers, chlorinated and brominated copolymer of isobutylene-isoprene (halobutyl rubber), chlorinated or sulfo-chlorinated polyethylene, copolymers of ethylene and chlorinated ethylene, epichlorohydrin
15 homo- and copolymers, especially polymers of halogen-containing vinyl compounds, for example polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polyvinylidene fluoride, as well as copolymers thereof such as vinyl chloride/vinylidene chloride, vinyl chloride/vinyl acetate or vinylidene chloride/vinyl acetate copolymers.
- 20 8. Polymers derived from α,β -unsaturated acids and derivatives thereof such as polyacrylates and polymethacrylates; polymethyl methacrylates, polyacrylamides and polyacrylonitriles, impact-modified with butyl acrylate.
9. Copolymers of the monomers mentioned under 9) with each other or with other unsaturated monomers, for example acrylonitrile/ butadiene copolymers, acrylonitrile/alkyl acrylate
25 copolymers, acrylonitrile/alkoxyalkyl acrylate or acrylonitrile/vinyl halide copolymers or acrylonitrile/ alkyl methacrylate/butadiene terpolymers.
10. Polymers derived from unsaturated alcohols and amines or the acyl derivatives or acetals thereof, for example polyvinyl alcohol, polyvinyl acetate, polyvinyl stearate, polyvinyl
30 benzoate, polyvinyl maleate, polyvinyl butyral, polyallyl phthalate or polyallyl melamine; as well as their copolymers with olefins mentioned in 1) above.

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11. Homopolymers and copolymers of cyclic ethers such as polyalkylene glycols, polyethylene oxide, polypropylene oxide or copolymers thereof with bisglycidyl ethers.
12. Polyacetals such as polyoxymethylene and those polyoxymethylenes which contain ethylene oxide as a comonomer.
- 5 13. Polyphenylene oxides and sulfides, and mixtures of polyphenylene oxides with styrene polymers or polyamides.
- 10 14. Polyurethanes derived from hydroxyl-terminated polyethers, polyesters or polybutadienes on the one hand and aliphatic or aromatic polyisocyanates on the other, as well as precursors thereof.
- 15 15. Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, for example polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12, 4/6, 12/12, polyamide 11, polyamide 12, aromatic polyamides starting from m-xylene diamine and adipic acid; polyamides prepared from hexamethylenediamine and isophthalic or/and terephthalic acid and with or without an elastomer as modifier, for example poly-2,4,4,-trimethylhexamethylene terephthalamide or poly-m-phenylene isophthalamide; and also block copolymers of the aforementioned polyamides with polyolefins, olefin copolymers, ionomers or chemically bonded or grafted elastomers; or with polyethers, e.g. with polyethylene glycol, polypropylene glycol or polytetramethylene glycol; as well as polyamides or copolyamides modified with EPDM or ABS; and polyamides condensed during processing (RIM polyamide systems).
- 20 25 16. Polyureas, polyimides, polyamide-imides, polyetherimids, polyesterimids, polyhydantoins and polybenzimidazoles.
- 30 17. Polyesters derived from dicarboxylic acids and diols and/or from hydroxycarboxylic acids or the corresponding lactones, for example polyethylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylcyclohexane terephthalate, polyalkylene naphthalate (PAN) and polyhydroxybenzoates, as well as block copolyether esters derived from hydroxyl-terminated polyethers; and also polyesters modified with polycarbonates or MBS.

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18. Polycarbonates and polyester carbonates.
19. Polyketones.
- 5 20. Polysulfones, polyether sulfones and polyether ketones.
21. Blends of the aforementioned polymers (polyblends), for example PP/EPDM, Polyamide/EPDM or ABS, PVC/EVA, PVC/ABS, PVC/MBS, PC/ABS, PBTP/ABS, PC/ASA, PC/PBT, PVC/CPE, PVC/acrylates, POM/thermoplastic PUR, PC/thermoplastic PUR, 10 POM/acrylate, POM/MBS, PPO/HIPS, PPO/PA 6.6 and copolymers, PA/HDPE, PA/PP, PA/PPO, PBT/PC/ABS or PBT/PET/PC.

The following examples illustrate the invention.

- 15 The antioxidant dispersions are prepared as described in US 5,116,534 using oleic acid and potassium hydroxide as surfactant. They have an active content of 40%..

Examples 1-3 and comparative example 2: stabilization and coagulation of an MBS graft latex

- 20 A calculated amount of the respective antioxidant dispersion is added at ambient temperature under stirring to a MBS latex. Stirring is continued for 5 minutes (magnetic stirrer, at approximately 1000 rpm). The stabilized MBS latex is filtered before coagulation. 210 g deionized water are mixed with 10.5% hydrochloric acid (10%) based on dry MBS, the mixture is then heated to 55°C. At this temperature and under stirring at 700 rpm, 150 g of 25 stabilized MBS graft latex (37.7% total solids content) are added within 1 to 2 minutes. Then the temperature is raised to 60°C (bath 73°C), maintained at this level for 5 minutes, then increased to 85°C (bath 103°C), and kept at this level for 5 minutes. The pH-value is measured. The mixture is filtered hot. The solid residue is taken up in 200 g deionized water at ambient temperature, filtered and washed with deionized water. The MBS graft powder is 30 then dried for 15 h at 60°C, approximately 150 mbar and airflow.

The thermal stability of the MBS powder so obtained is determined with a DSC apparatus under oxygen atmosphere. The time until the maximum of the exothermic reaction at 180°C

is reached is determined. The exothermic reaction, which occurs, is a measure of the degradation of the polymer.

The stabilization of the different MBS powders obtained, and their thermal stability is shown

5 in Table 1

Table 1: Thermal stability of stabilized MBS powder

Example	Additive 1	Conc.*	Additive 2	Conc.*	Thermal stability**
Comparative 1***	@Irganox 1076	0.2%	DLTDP	0.6%	35 minutes
Comparative 2	@Irganox 245	0.3%	DLTDP	0.9%	283 minutes
Inventive 1	@Irganox 3790	0.3%	DLTDP	0.9%	388 minutes
Inventive 2	@Irganox 415	0.3%	DLTDP	0.9%	454 minutes
Inventive 3	@Wingstay L	0.3%	DLTDP	0.9%	350 minutes

* additive concentrations are weight-% based on dry MBS powder.

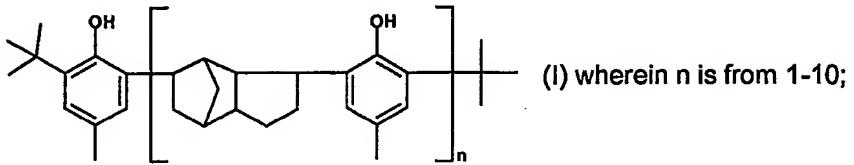
10 ** thermal stability DSC, 180°C, oxygen, aluminum cups: minutes to the maximum of the exotherm.

***Comparative example 1 is coagulated with 1.21% sulfuric acid (6.8g 10% sulfuric acid) based on dry MBS.

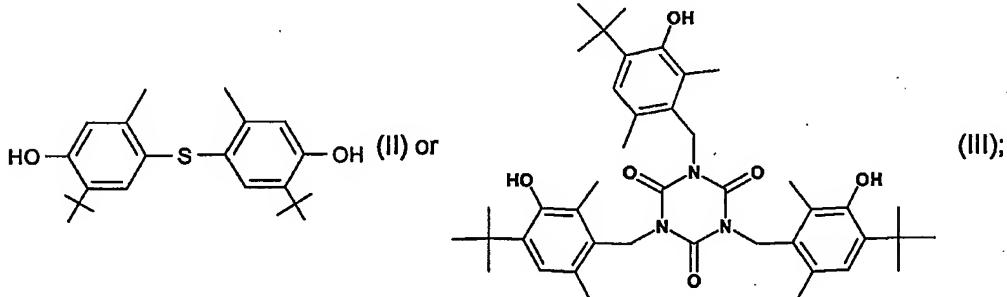
Claims

1. A stabilized polymer composition comprising

- a) a polymer, which is a graft copolymer of methylmethacrylate and styrene on
 5 polybutadiene or polybutadiene-styrene (methylmethacrylate-styrene-butadiene graft copolymer MBS);
 b) a sterically hindered phenolic antioxidant of formula (I), (II) or (III) or a mixture thereof



10



and

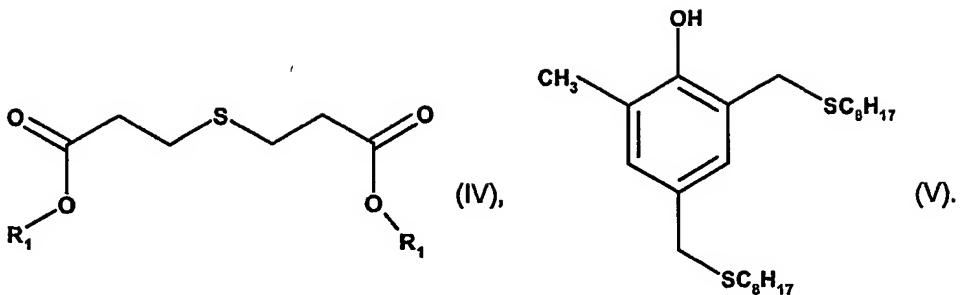
- c) a thioether differing from that of formula (II);

with the proviso, that no other styrene polymer or copolymer, which is not a graft copolymer
 15 on butadiene is present.

2. A stabilized polymer composition according to claim 1, which is in the solid state.

3. A stabilized polymer composition according to claim 2, which is in the form of a powder or
 20 granulate.

4. A stabilized polymer composition according to claim 1 wherein the thioether is a compound of formula (IV) or (V)



wherein the R₁ are independently C₈-C₂₀alkyl.

5. A stabilized polymer composition according to claim 1 wherein the sterically hindered phenolic antioxidant is present in an amount of 0.05 to 1% based on the weight of the dry graft copolymer, component a).

6. A stabilized polymer composition according to claim 1 wherein the thioether is present in an amount of 0.1 to 5% based on the weight of the dry graft copolymer, component a).

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7. A stabilized polymer composition according to claim 1 wherein the ratio of sterically hindered phenolic antioxidant to thioether is from 1:1 to 1:5.

15

8. A stabilized polymer composition according to claim 1 comprising additionally a further sterically hindered phenolic antioxidant different from that of claim 1, a phosphite process stabilizer, a UV-absorber, a sterically hindered amine light stabilizer, a metal deactivator, an acid scavenger, a metal salt of a fatty acid, a fluorescent whitening agent, a biocide or a surfactant.

20

9. A process for the stabilization of a graft copolymer of methylmethacrylate and styrene on polybutadiene or polybutadiene-styrene (methylmethacrylate-styrene-butadiene graft copolymer MBS) where no other styrene polymer or copolymer, which is not a graft copolymer on butadiene is present, comprising the steps

25

a) adding to the MBS latex a sterically hindered phenolic antioxidant of formula (I), (II) or (III) and a thioether according to claim 1;

b) coagulating the MBS latex and

c) drying the MBS latex at elevated temperature.

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10. A process according to claim 9 wherein the drying step is carried out at a temperature of 40° C to 150° C.
11. Use of a sterically hindered phenolic antioxidant of formula (I), (II) or (III) together with a
5 thioether for the stabilization of a graft copolymer of methylmethacrylate and styrene on polybutadiene or polybutadiene-styrene (methylmethacrylate-styrene-butadiene graft copolymer MBS) where no other styrene polymer or copolymer, which is not a graft copolymer on butadiene is present.
- 10 12. Use of a stabilized MBS graft copolymer according to claim 9 as impact modifier for polymers.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/051983

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08F279/06 C08K5/13 C08K5/375 C08K5/3492 C08K5/36
 C08K5/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C08F C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 488 550 A (ROHM & HAAS) 3 June 1992 (1992-06-03) cited in the application the whole document	1-12
X	US 5 116 534 A (MOLLET HANS ET AL) 26 May 1992 (1992-05-26) cited in the application the whole document column 4, line 34 - line 57	1-12
X	US 2003/144395 A1 (BROUSSARD ET AL.) 31 July 2003 (2003-07-31) the whole document	1-12
A	EP 0 668 318 A (ROHM & HAAS) 23 August 1995 (1995-08-23) the whole document	1-12

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the International search

Date of mailing of the International search report

10 February 2005

17/02/2005

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